

10/527441

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number
WO 2004/024373 A1

(51) International Patent Classification⁷: **B22F 1/02**,
9/26, 3/11

(21) International Application Number:
PCT/EP2003/009552

(22) International Filing Date: 20 August 2003 (20.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02078736.2 10 September 2002 (10.09.2002) EP
60/409,990 12 September 2002 (12.09.2002) US

(71) Applicant (*for all designated States except US*): UMI-
CORE [BE/BE]; Rue du Marais 31, B-1000 Brussels (BE).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): YUAN, Ding
[CA/CA]; 958 Rice Road, Edmonton, AB T6R 1A1
(CA). AMINIAN, Hossein [CA/CA]; 6 Deacon Place, St.
Albert, AB, T8N 6S5 (CA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

— *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: NI-COATED TI POWDERS

(57) Abstract: The present invention relates to coated powder, comprising a Ti-bearing core and a Ni-bearing coating, which can be used for the production of porous Ni-Ti articles by the self-propagating high temperature synthesis (SHS) method. The obtained articles are ideally suited for use in biomedical applications. According to the invention, a coated powder is used comprising a metallic Ti-bearing core and a metallic Ni-bearing coating, ' characterised by a Ni:Ti atomic ratio of more than 0.5, preferably between 0.9 and 1.1, and more preferably between 0.96 and 1.04. By using coated powders, local fluctuations in composition are limited and well under control. Milling of powders and the ensuing contamination risks are avoided. The sintered objects obtained using coated powders have a more homogeneous porosity than that using mixed Ni and Ti powders.

BEST AVAILABLE COPY

WO 2004/024373 A1

Ni-coated Ti powders

The present invention relates to coated powder, comprising a Ti-bearing core and a Ni-bearing coating, which can be used for the production of porous Ni-Ti alloys.

Such a porous Ni-Ti alloy article is described in U.S. Pat. No. 5,986,169. The article has a porosity of 8 to 90 % and is defined by a network of interconnected passageways extending throughout. The network exhibits an isotropic permeability permitting complete migration of fluids. The material is elastically deformable. These characteristics render it useful in biomedical and other applications. For producing the porous article, the so-called self-propagating high-temperature synthesis (SHS) method is used in which the alloy is produced by means of a layered combustion which exploits exothermic heat emitted during interaction of elemental nickel and titanium powders.

U.S. Pat. No. 2,853,403 describes a method for producing composite metal powders. This method consists of dispersing, in solid form, particles of one or more metals of interest as nuclei in an ammoniated solution in which another metal of interest having different chemical and/or physical properties is present as a soluble salt, and precipitating the latter metal from the solution by gas reduction to form composite metal particles in which the dispersed metal particles are coated by the precipitated metal. This method was however never specifically applied for the manufacture of Ni-coated Ti powder.

The use of elemental Ni and Ti powders renders the production process sensitive to segregation problems, resulting in composition fluctuations and/or non-homogeneous porosity. Composition fluctuations can in turn lead to the formation of unwanted secondary phases.

According to the invention, the above drawbacks can be overcome using coated powder, comprising a metallic Ti-bearing core and a metallic Ni-bearing coating, characterised by a Ni:Ti atomic ratio of more than 0.5, preferably between 0.9 and 1.1, and more preferably between 0.96 and 1.04. Atomic ratios of more than 0.5 to about 1 are

preferred as this avoids the formation of secondary phases and yields an alloy with better mechanical properties.

5 The Ti-bearing core may consist of pure Ti, while the Ni-bearing coating can consist of pure Ni.

10 It may be useful to mix Ti-bearing powder or Ni-bearing powder with the coated powder so as to obtain a Ni:Ti atomic ratio of the mixture of between 0.9 and 1.1, and preferably between 0.99 and 1.01. This procedure allows for easy adjustments to the Ni:Ti ratio.

The particle size of the powders should preferably be finer than 150 mesh.

15 Above described powders can be used for the manufacture of sintered objects, possibly using the SHS technique.

Another object of the invention concerns a process of manufacturing a coated powder comprising the steps of:

- 20 - providing for suitable quantities of a Ti-bearing powder and of a Ni salt bearing aqueous solution;
- feeding said powder and said solution in an autoclave together with a quantity of NH_4OH , and, optionally, with a quantity of ammonium salts;
25 - precipitating the Ni onto the Ti-bearing powder by hydrogen reduction;
- washing, filtering and drying the slurry obtained, thereby obtaining a Ni-coated Ti powder.

30 The Ni is preferably precipitated onto the Ti-bearing powder at a temperature of at least 100 °C and a hydrogen pressure in the autoclave of at least 1.4 MPa.

35 Powders obtained by this coating process are, as such or after mixing with Ni-bearing or Ti-bearing powders, suitable for SHS sintering of objects.

40 By using coated powders, local fluctuations in composition are limited and well under control. Ni-coated Ti powder also decreases the diffusion distance between the Ni and Ti atoms, which may

eliminate or reduce the formation of unwanted intermetallic compounds such as Ni_3Ti and NiTi_2 . It has been found that the porosity of the porous titanium-nickel produced by SHS starting from Ni-coated Ti powder is more homogeneous throughout the sample compared to starting with elemental powders. It has also been found that the compactibility of Ni-coated Ti powder is significantly better than that of elemental powders. Because of this, next to the possibility for a decreased die wear, larger devices can be produced. Additional advantages are that no milling is required, thus avoiding contamination such as oxidation of Ti during the preparation stage, and that the intimate contact between Ni and Ti makes it possible to perform SHS with no or less preheating compared to green compacts made of elemental Ti and Ni powders.

The SHS process can produce Ni-Ti alloys with large pore volumes and a three-dimensional interconnected network of pores and channels. This porous network is particularly suitable for implants to achieve secure tissue-to-implant bonding. Pre-alloyed powder, such as atomised Ni-Ti, does not work for the SHS process, since it is already an alloy and the exothermic reaction does not take place during sintering.

During the manufacturing the coated powder, 50 to 500 g/l ammonium salts, such as $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{CO}_3$, may be added, to prevent the formation of unwanted $\text{Ni}(\text{OH})_2$ and to ensure a smooth coating.

The following Figures illustrate the invention.

Figure 1 shows an SEM of coated product.

Figure 2 shows an EDS map of the cross section of Ni-coated Ti powder; the solid Ti cores (left) and the Ni-coating (right) are visible.

Figure 3 gives a longitudinal view of powder A after compaction and SHS; the arrow indicates the direction of the propagation front.

Figure 4 is a SEM-image of powder A (left) and powder B (right) after SHS.

Figure 5 shows an XRD spectrum of Ni-coated powder D after SHS.

Figure 6 shows macroscopic pictures of samples made by the SHS process using different raw materials: (a) using powder D, (b) powder E, (c) powder F, (d) powder G.

Figure 7 shows SEM pictures of samples made by SHS using various raw materials at low (top) and high (bottom) magnification: (a) and (d) for powder D, (b) and (e) for powder F, (c) and (f) for powder G.

5

Preferred embodiment 1

Ti powder along with a Ni bearing solution, such as a sulphate or a carbonate, and, in particular when a sulphate is used, ammonium hydroxide (ammoniac), preferably in a $\text{NH}_3\text{:Ni}$ ratio of 2:1, are fed to an autoclave. A surface-active additive, such as anthraquinone, is also added to the solution to an amount of 0.2 to 5 wt.% of the Ti powder. This ensures a smooth coating of the Ti particles. The Ni is then precipitated on the titanium surface using H_2 at a temperature of 100 to 200 °C and at an H_2 pressure of 1.4 to 3.4 MPa. After coating, the slurry is washed, filtered and dried.

Example 1

The result of coating a batch of Ti powder as described in preferred embodiment 1 is given in Table 1. The reduction temperature was 150 °C and the reduction pressure was maintained at 3.4 MPa. A SEM (Scanning Electron Microscope) picture of the coated product is shown in Figure 1. An EDS (Energy Dispersive Spectroscopy) map of the cross section of the powder is shown in Figure 2. SEM and EDS maps show a homogeneous and smooth coating.

Table 1: Results of coating

Feed		Coated powder	
Ni (g/L)	Ti (g/L)	Ni wt. %	Ti wt. %
21.8	21.6	53.2	46.6

Example 2

Ni-coated Ti powder was produced starting from 3 types of Ti powder having a different particle size distribution:

- powder A: Ni coated -400 mesh Ti powder;
- powder B: Ni coated -250 +325 mesh Ti powder;
- powder C: Ni coated -150 +200 mesh Ti powder.

The composition of the coated powder is shown in Table 2.

Table 2: Composition of the coated powder

Powder reference	Composition	
	Ni wt. %	Ti wt. %
A	53.8	45.8
B	53.7	46.1
C	53.3	46.0

5

Example 3

The three different powders were die-compacted on an Instron-press to a density of respectively 48 %, 59 % and 51 % of the theoretical density using a compaction load of 22 kN, 19 kN and 11 kN

10 respectively.

SHS performed on compacted powder A requires an ignition time of less than 10 seconds. The propagation front is parallel and stable and the resulting sample dimensions are also stable (Figure 3). Powders B and C showed a tendency to more intensive melting in the upper part of the sample.

Two types of pores are present: small ones and large elongated ones perpendicular to the propagation front direction (Figure 4). As the initial particle size increases from powder A to powder C, the width of the elongated pores increases from roughly 200-300 μm to 400-600 μm and finally to 800-1000 μm . The porosity distribution in each sample is homogeneous, except in the regions where a large amount of liquid phase was present, resulting in lower porosity.

25

The phases present in the SHS-product have been determined using XRD (X-Ray Diffraction) and EDX (Energy Dispersive X-ray) analysis. The XRD diagram in Figure 5 clearly shows the presence of the desired Ni-Ti phase, both monoclinic and cubic, and possibly a limited amount of NiTi_2 .

30

Example 4

To be able to compare Ni-coated Ti powder with elemental Ni and Ti powders, the following batches were prepared:

- powder D: Ni coated -400 mesh Ti powder, blended with some additional Ni powder;
- powder E: Ni coated -250 +325 mesh Ti powder, blended with some additional Ni powder;
- powder F: Ni coated -150 +200 mesh Ti powder, blended with some additional Ni powder;
- powder G: Ni powder of 1.2 μm (d_{50}), mixed with -250 +325 mesh Ti powder in a 1:1 atomic ratio (55.07:44.93 Ni:Ti wt.% ratio).

Based on the composition analysis of the Ni-coated Ti powder, additional fine Ni powder was blended with the coated powder to balance the Ni:Ti atomic ratio to 1:1. The addition of Ni powder is shown in Table 3.

Table 3: Amount of Ni added to 100 g of Ni-coated Ti powder

Powder reference	Ni:Ti (wt.%)	Ni powder added (g)
D	53.8:45.8	2.34
E	53.7:46.1	2.80
F	53.3:46.0	3.08

Quartz tubes with a diameter of 20 to 25 mm and a length of 130 to 170 mm were used for containing the powder. Powder mixture G was ball milled for 2 hours before being loosely packed in a quartz tube. Green density of the mixed powder was about 50 to 60 %. A load of 30 to 40 kN was needed to press the sample.

The green densities for powders D, E and F were respectively about 45%, 50% and 65%, accomplished using loads of 10 kN, 15 kN and 18 kN respectively.

All samples were placed in a vacuum chamber with a vacuum of about 0.01 Pa. After pre-heating the samples to 350 °C for 1 hour, the samples were ignited. SHS took place.

Figure 6 shows macroscopic pictures of the samples prepared by SHS. The surface morphology of the samples made by Ni-coated Ti powder was

homogeneous. The surface morphology of the samples made by mixed Ni and Ti powders was rough and the porosity was inhomogeneous.

- 5 SEM pictures in Figures 7(c) and 7(f) show that the pore size and morphology of the sample made from mixed Ni and Ti powder are inhomogeneous. Figures 7(a), 7(b), 7(d), and 7(e) show that the pore size and morphology prepared from finer Ni-coated Ti powders are more homogeneous than those by coarser Ni-coated Ti powder. There are also more open pores in the samples using finer Ni-coated Ti powders.
- 10 Overall, samples using Ni-coated Ti powder have a more homogeneous porosity than that using mixed Ni and Ti powders.

Claims

1. Coated powder, comprising a metallic Ti-bearing core and a metallic Ni-bearing coating, characterised by a Ni:Ti atomic ratio of more than 0.5, preferably between 0.9 and 1.1, and more preferably between 0.96 and 1.04.
2. Coated powder according to claim 1, wherein the Ti-bearing core consists of metallic Ti and the Ni-bearing coating consists of metallic Ni.
3. Powder mixture comprising coated powder according to claims 1 or 2, further comprising one or both of Ni-bearing powder and Ti-bearing powder, wherein the Ni:Ti atomic ratio of the mixture is between 0.9 and 1.1, preferably between 0.99 and 1.01.
4. Coated powder or powder mixture according to any one of claims 1 to 3, characterised by a particle size finer than 150 mesh.
5. Use of a coated powder or a powder mixture according to any one of claims 1 to 4 for the manufacture of a sintered body.
6. Use of a coated powder or a powder mixture according to claim 5, characterised in that the sintered body is obtained by a self-propagating high temperature process.
7. A sintered body obtainable by a self-propagating high temperature process using powders according to any one of claims 1 to 4.
8. Process of manufacturing a coated powder according to claims 1 or 2, comprising the steps of:
 - providing for suitable quantities of a Ti-bearing powder and of a Ni salt bearing aqueous solution;
 - feeding said powder and said solution in an autoclave together with a quantity of NH_4OH , and, optionally, with a quantity of ammonium salts;
 - precipitating the Ni onto the Ti-bearing powder by hydrogen reduction;

- washing, filtering and drying the slurry obtained, thereby obtaining a Ni-coated Ti powder.

- 5 9. Process according to claim 8, whereby the Ni is precipitated onto the Ti-bearing powder at a temperature of at least 100 °C and a hydrogen pressure in the autoclave of at least 1.4 MPa.
- 10 10. Process of manufacturing a coated powder according to claim 3, comprising the steps of claim 8, and further comprising the step of intimately mixing the Ni-coated Ti powder with one or both of Ni-bearing and Ti-bearing powder.
- 15 11. Process of manufacturing a porous sintered body based on a Ni-Ti alloy, comprising the steps of any one of claims 8 to 10, and further comprising the step of subjecting the powder or powder mixture to a self-propagating high temperature synthesis operation.
12. A sintered body obtainable by a process according to claim 11.



Fig. 1

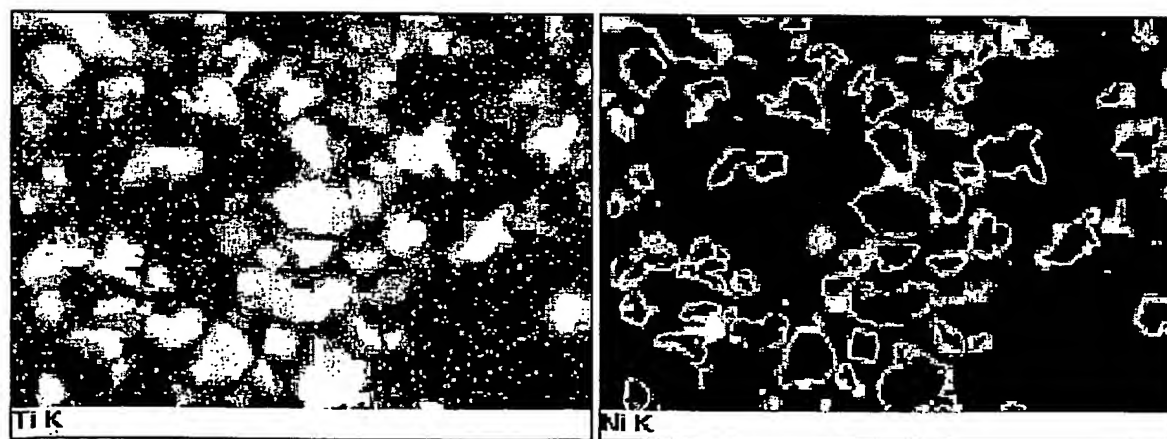


Fig. 2

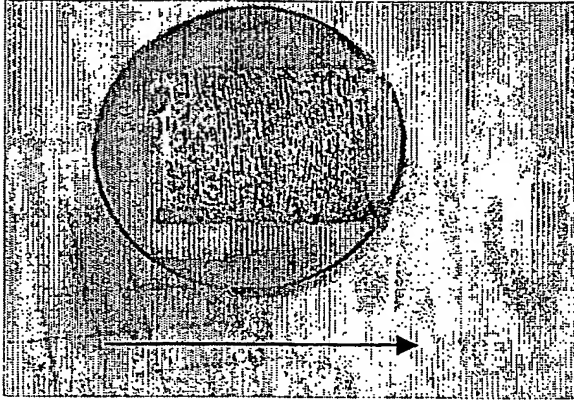


Fig. 3

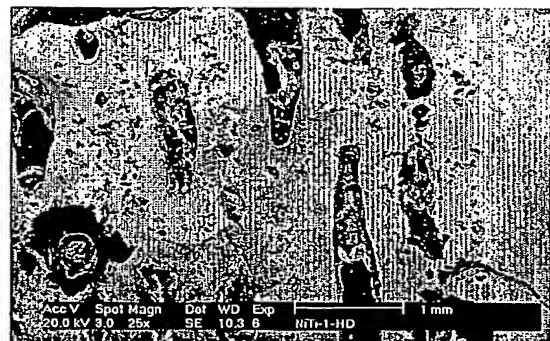
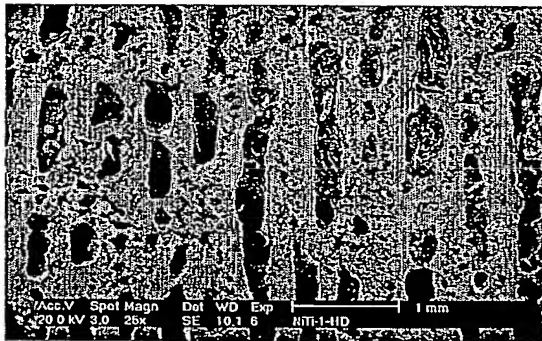
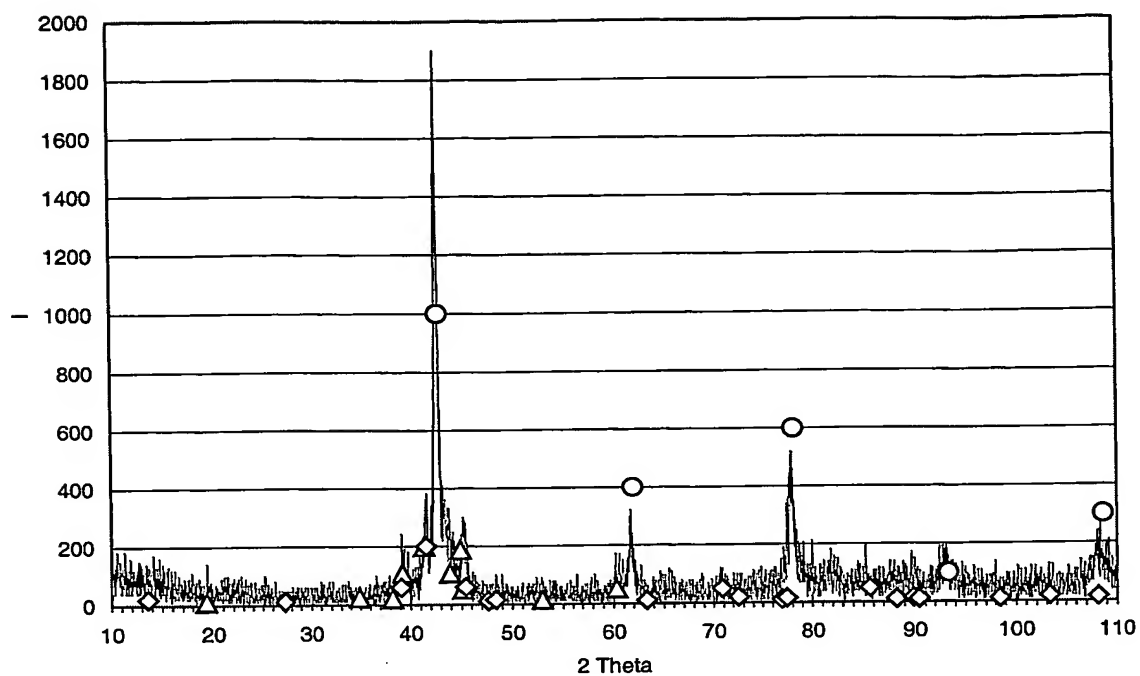


Fig. 4

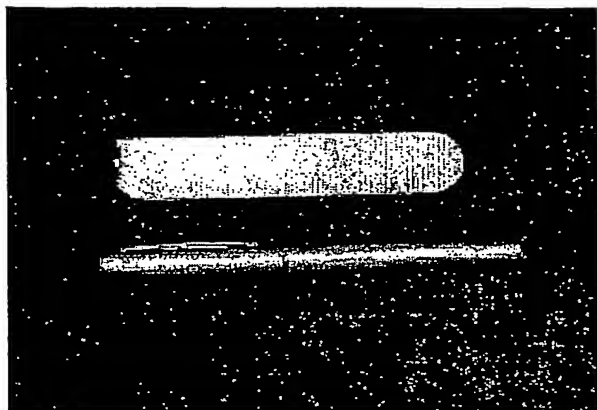


○ NiTi bcc

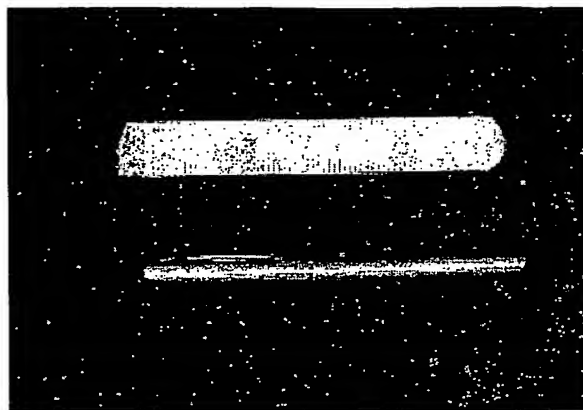
△ NiTi monoclinic

◇ NiTi₂

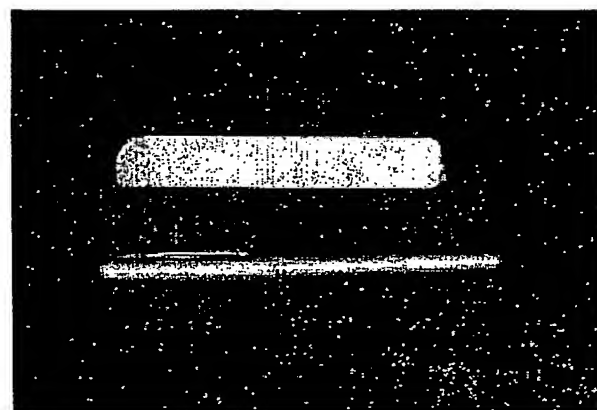
Fig. 5



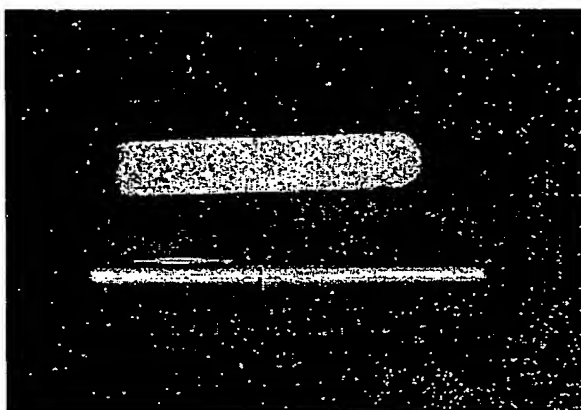
(a)



(b)



(c)



(d)

Fig. 6

Rec'd PCT/PTO 10 MAR 2005
10/527441

INTERNATIONAL SEARCH REPORT

International Classification No
PCT/EP 03/09552

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B22F1/02 B22F9/26 B22F3/11		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 B22F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) PAJ, EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 632 (C-1280), 2 December 1994 (1994-12-02) -& JP 06 240381 A (KAWASAKI STEEL CORP), 30 August 1994 (1994-08-30) abstract	1,2,4,5
Y		8,9
A		7
Y	US 2 853 403 A (BRYAN HAWORTH JOHN ET AL) 23 September 1958 (1958-09-23) cited in the application column 2, line 16 column 2, line 34	8,9
	-/--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 January 2004		Date of mailing of the international search report 04/02/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Lilimpakis, E

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/09552

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 02, 28 February 1997 (1997-02-28) - & JP 08 284622 A (MITSUBISHI MATERIALS CORP), 29 October 1996 (1996-10-29) abstract	1, 2, 4
A	WO 01 87370 A (VIDAM TECHNOLOGY LTD ; VALBRI BIO INC (CA); DAMBAEV GEORGIY TSYRENOV) 22 November 2001 (2001-11-22) the whole document	3-7, 10-12
A	DATABASE WPI Section Ch, Week 0155 Derwent Publications Ltd., London, GB; Class M, Page 22, AN 2001-501429 XP002228912 - & RU 2 170 645 C (DAMBAEV G TS ET AL), 20 July 2001 (2001-07-20) abstract	3, 5-7, 10-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

PCT/EP 03/09552

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 06240381	A	30-08-1994	NONE	
US 2853403	A	23-09-1958	NONE	
JP 08284622	A	29-10-1996	NONE	
WO 0187370	A	22-11-2001	CA 2308898 A1 AU 6194301 A WO 0187370 A1	19-11-2001 26-11-2001 22-11-2001
RU 2170645	C	20-07-2001	RU 2170645 C2	20-07-2001

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.